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ABSTRACT

Thin-film CdS is used as a window layer in most of the current thin-film polycrystalline device technologies including absorbers based on cadmium telluride (CdTe) and copper indium selenide (CIS) and copper indium gallium selenide (CIGS). Device performance has been linked to the deposition technique and posttreatment of the CdS layer. Here we used the radio frequency photoconductive decay (RFPCD) technique to measure the photoconductive lifetime of CdS that had been deposited by various techniques. This includes chemical bath deposition (CBD) and laser deposition. CdCl₂ treatment increases the photoconductive response and reduces shallow trapping effects. In addition, tellurium doping was found to significantly decrease the photoconductive response, as well as the hole lifetime, below that of the undoped material. The impact of these CdS properties on device performance will be discussed.

INTRODUCTION

Thin-film CdS is an integral component of solar cells based on CdTe, and CIS or CIGS. The CdS serves as an n-type window in a window/absorber heterojunction and primarily functions as a material needed for junction formation. Because of the apparently short base-diffusion length in all of the above materials, the heterojunctions have produced much better efficiencies than homojunctions. On the other hand, the CdS produces little to no current in spectral response data reported for these devices. However, CdS is a well-established photoconducting material and the reasons for the apparent "dead layer" properties in solar cells have not been understood. Here, we have measured the photoconducting properties of CdS films produced by various growth techniques. Some of the films have been processed by a CdCl₂-annealing step. Another set of films grown by sputtering has been doped with various levels of tellurium. The latter was done because it has been recently reported that Te diffusion into the CdS is common in the CdS/CdTe device. We will show that the effects of both CdCl₂ annealing and sulfur/tellurium interdiffusion on the photoconductive properties of CdS is very significant.

EXPERIMENTAL TECHNIQUE

Lifetime and Photoluminescence Measurement

The recombination lifetime was measured by the recently described RFPCD apparatus [1]. Excess carrier gen-

eration was produced by a tripled yttrium aluminum garnet (YAG) laser, equipped with a wavelength tripler, producing 355-nm pulses of about 3 ns full width half maximum (FWHM). Low temperature measurements were performed in a second generation RFPCD apparatus that uses an operating frequency of about 900 MHz. The excess carrier generation was produced by white light from a small, pulsed xenon flash lamp.

The energy-resolved photoluminescence (PL) measurements were made using a continuous wave (cw) helium-cadmium laser. The PL spectra were analyzed using a grating-dispersion element in conjunction with a charge-coupled device detector for parallel collection of the entire emission spectrum.

CdS Films Grown by Chemical-Bath Deposition

The first set of samples to be described were grown at Colorado School of Mines by CBD. The thickness of these films was either 1200 Å or 2000 Å, and they were deposited on SnO₂-coated glass substrates. The films were deposited from an alkaline solution containing cadmium acetate, ammonium acetate, ammonium hydroxide, and thiourea [2]. The films in the CSM solar cell were coated with CdCl₂ and then annealed in an N₂ atmosphere at 450° C prior to the CdTe deposition. This processing boosts the spectral response in the 500 to 600-nm range and J_{SC} by about 2.7 ma/cm².

EXPERIMENTAL RESULTS

Fig. 1. shows the energy resolved PL of two CBD-grown films. Film B was subjected to the standard CdCl₂-annealing process, whereas Film A was unannealed. The data show that film A has very weak PL emission with little to no emission corresponding to the band-to-band transition at 2.53 eV [3]. However, the emission from the CdCl₂-annealed film shown in Curve B has much stronger emission with significant intensity corresponding to the intrinsic transition at 2.53 eV. These data indicate that the unannealed film is dominated by defects, whereas the annealed film shows some recombination from free electrons and holes.

Fig. 2 shows the RFPCD response of two films using the tripled YAG wavelength of 355 nm as the excitation source. Film B was subjected to the standard CdCl₂-annealing process, whereas Film A was unannealed. These films show the photoconductive-decay behavior that is assumed to be a trap-limited response [4] with a long-term

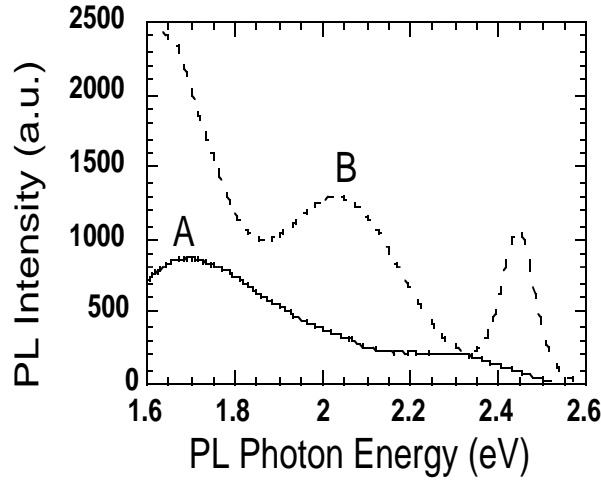


Fig. 1. The energy-resolved PL of CdS films grown by CBD. Curve A: Spectra of as-grown sample. Curve B: Spectra of CdCl_2 -annealed sample.

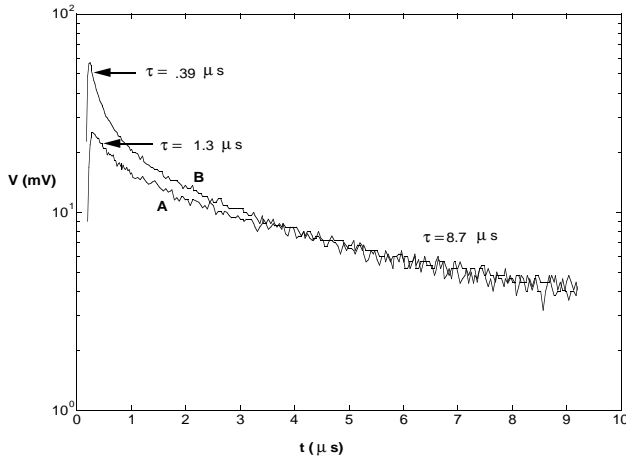


Fig. 2. Photoconductive decay of the samples of Fig. 1 grown by CBD. Curve A: photoconductive decay spectra of as-grown sample. Curve B: photoconductive decay of CdCl_2 -annealed sample. The pulsed-excitation wavelength is 355 nm.

decay time of about 9 μs . This assumption is made because the film is a fine-grain polycrystalline material and the recombination lifetime is likely to be much shorter than the microsecond decay times observed here. The annealed Film B shows an enhanced photoresponse near $t=0$ with an initial lifetime of 0.39 μs . This response is indicative of trap filling, with an initial response that may be indicative of the recombination lifetime. By contrast, Film A has a weaker response that may be indicative only of trap capture and emission. The effect of CdCl_2 treatment on the response of these films is likely to be increased grain size because this is a well-known flux for grain growth.

To test the shallow trapping explanation of these data, the RFPCD measurements were performed at temperatures between 80 and 300 K with a new apparatus to be described

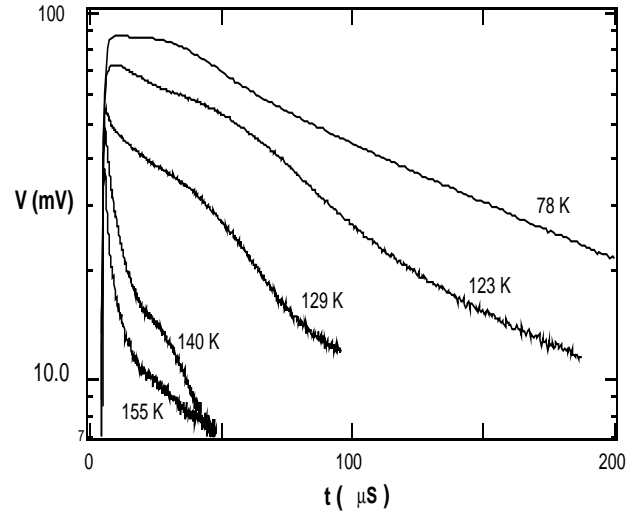


Fig. 3. Photoconductive decay of CBD-grown CdS (film B) at five ambient temperatures between 78 and 155 K. The pulsed-excitation source was a pulsed xenon flash lamp.

later [5]. The probe frequency for the new variable-temperature apparatus is about 900 MHz. Fig. 3 shows the photoconductive decay of the annealed sample B over the temperature range of 78 to 155 K. There is a steep increase in the long-term decay time with increasing temperature that is similar to the trap emission [6,7] commonly observed in polycrystalline CdTe. In a sense, this photoconductive decay behavior is similar to that seen by capacitance techniques in deep-level transient spectroscopy (DLTS) experiments.

A somewhat unusual effect is seen in the photoconductive decay in the temperature range from 175 to 296 K and shown in Fig. 4. Here the initial decay rate (near $t=0$) actually increases with increasing temperature. The slow decay is present and increases in amplitude as the temperature

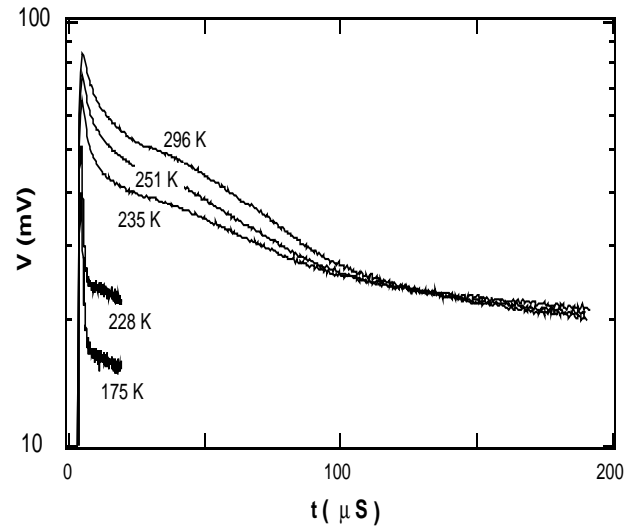


Fig. 4. Photoconductive decay of CBD-grown CdS-film B at five ambient temperatures between 175 and 296 K. The pulsed-excitation source was a pulsed xenon flash lamp.

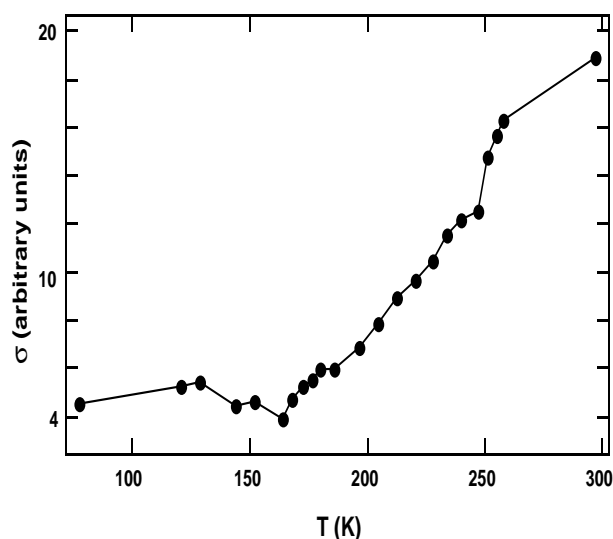


Fig. 5. Dark conductivity of CBD-grown CdS-film B as a function of temperature from 80 to 296 K. Conductivity is measured by radio-frequency photoconductivity and is presented in arbitrary units.

increases. These data can be explained by assuming that a strong recombination mechanism becomes active near 175 K. In this model, the trapping-capture cross section increases with temperature so that trapping dominates the photoconductive behavior near room temperature.

This behavior is compatible with the dark-conductivity data of the same film that is shown in Fig. 5. Here the RFPCD-test system is set up such that the dark conductivity is balanced at 78 K and then measured as a function of temperature. At about 175 K, the dark conductivity begins increasing with temperature. The dark conductivity increases by about a factor of 5 between 150 and 296 K. This effect can be related to donor activation and/or some combination of deep-level defect interaction with the free carriers. To further identify the defect processes involved here, more detailed measurements are being undertaken.

In summary, we found that the photoconductive decay is greatly enhanced by CdCl₂ annealing. The photoconductive response is fairly strong and limited by shallow trapping in CBD-grown films.

Tellurium-Doped CdS

A second set of samples was grown by pulsed-laser deposition at the University of Toledo at 360° C. All samples were grown from pressed-powder targets starting from the same batch of material. All samples shown here were treated with CdCl₂ at 400° C for 20 minutes. The RFPCD response (355 nm) is shown in Fig. 6. Sample A is "pure" CdS; i.e., no Te was added to the starting material. Sample B is CdS with 0.1-mole percent Te added. The effect of Te doping is quite apparent from these data. The amplitude of the photoconductive signal is reduced by about an order of magnitude. The initial lifetime of the Film A is 0.29 μs, whereas it re-

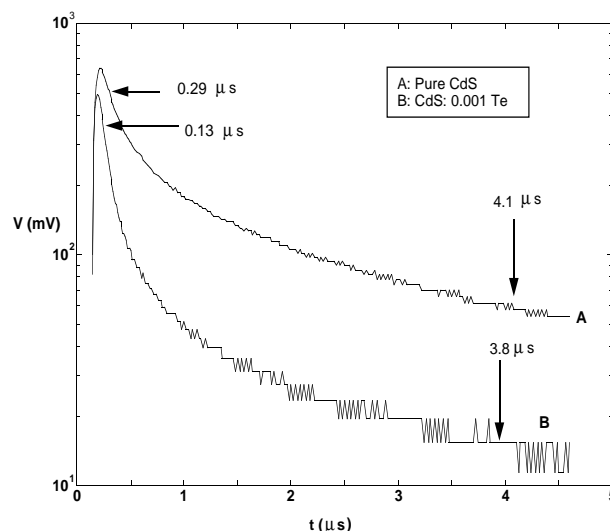


Fig. 6. Photoconductive decay of two CdS grown by laser deposition. Curve A: CdS film that is undoped. Curve B: CdS film with the addition 0.1 mole-percent Te.

duces to about 0.13 μs for Film B. The effect of Te is therefore to trap holes and act as either deep traps or recombination centers. Higher incorporations of Te further reduced the photoresponse of the CdS so that, at 1.0-mole percent, the latter was very weak.

CONCLUSIONS

In the CdS/CdTe solar cell, CdCl₂ annealing has proven to be essential to making high-performance cells, and interdiffusion appears to be a consequence of that annealing. One effect of annealing appears to be improved open-circuit voltage. As the lattice mismatch between CdS and CdTe is about 9 percent, a defect layer at the interface produces large increases in J_0 . That defect layer is likely reduced by interdiffusion resulting in large V_{OC} . The consequence of interdiffusion is that the photoresponse of the CdS is destroyed so that current response from the window layer is negligible. The effect of CdCl₂ annealing is to greatly increase the photoconductive response of CdS films grown by all of the common techniques. Another likely mechanism of CdCl₂ annealing is grain growth in the film and decreased grain boundary trapping and recombination.

These effects on PV performance have been modeled using the SimWindows [8] program with a defect layer incorporated at the interface. An interface defect layer is critical to obtaining the values of open-circuit voltage obtained in state-of-the-art solar cells. Without the latter, the modeled open-circuit voltage is much too large. The interplay between open-circuit voltage and current response from the CdS window layer could be important in developing improved devices.

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